

THE FLUORESCENCE AND MAGNETIC
ROTATION SPECTRA OF
POTASSIUM VAPOR

BY

T. S. CARTER

(DISSERTATION FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
AT JOHNS HOPKINS UNIVERSITY)

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INTRODUCTION.

RECENT study of the optical properties of sodium vapor¹ by one of the present writers, has shown that our knowledge of the structure of the molecule and of the mechanism of radiation may be increased by the investigation of metallic vapors at comparatively low temperatures. During the investigation the periodicities of the vibrating mechanisms were studied in a number of ways : by absorption, by exciting the vapor with white or monochromatic light, by cathode ray stimulation, and from the standpoint of the magneto-optical properties of the vapor. The fluorescence spectrum which appears when the non-luminous vapor is stimulated by white light, is very complex, and resembles many emission band spectra.

A method was found, however, by which it was possible to analyze this complex spectrum into a number of simpler spectra, each one of which could be made to appear at will by exciting the vapor with a monochromatic source of radiation of the proper frequency. The vapor can be excited to fluorescence by monochromatic sources obtained by utilizing certain lines from the arcs of various metals such as zinc, cadmium, thallium, lead, silver, bismuth and copper. In each case a series of lines is obtained, the lines of the series being very nearly equidistant.

It was further found that any given series of lines could be brought out by exciting the fluorescence with a source of radiation of wavelength corresponding to that of any line in the series, but that certain lines were sometimes absent depending upon the point of excitation.

Sodium vapor in a strong magnetic field has the property of

¹ R. W. Wood, *Phil. Mag.*, Nov., 1906.

rotating the plane of polarization of light for wave-lengths corresponding to those of certain lines in its absorption spectra, *i. e.*, polarized light, which has been passed through magnetized sodium vapor and a Nicol's prism (set originally for the complete extinction of light) gives a bright line spectrum consisting of a large number of sharp lines. Each bright line corresponds to a dark line in the absorption spectrum (or more exactly to wave-lengths very close to it) but it was found only a very small percentage of the absorption lines showed, this rotatory power. There are only about 100 strong lines in this spectrum, which has been called the magnetic rotation spectrum, while there are some 2,500 lines in the same region in the absorption spectrum. The magnetic rotation spectrum resembles very closely the fluorescent spectrum excited by white light, although there are fewer lines in it. The intensities of the lines are very variable, and apparently bear no relation to the intensities of the corresponding absorption lines.

Five or six distinct series of equidistant lines have been identified in the magnetic rotation spectrum, and these appear to correspond to the series in the fluorescent spectrum brought out by monochromatic stimulation, though they are not coincident with any which have been obtained thus far.

In view of the similarity between the emission spectra of sodium and potassium, it was thought very desirable to extend to potassium vapor studies along the same line.

HISTORICAL.

The red fluorescence which is exhibited by the vapor of metallic potassium when it is illuminated with a beam of white light was first observed by Wiedemann & Schmidt.¹

The metal was enclosed in an exhausted glass bulb heated until vaporization occurred, and a strong beam of sun or arc-light focused at the center of the bulb. A red cone of fluorescent light appeared, which, when examined with the spectroscope, showed a red band, the position of which as roughly determined was between wave-lengths 695 and 615 $\mu\mu$.

¹ Wied. Ann., 57, 447, 1896.

GENERAL FACTS.

The vapor has been studied from the standpoint of its absorption, fluorescence, and selective magnetic rotation of the plane of polarization, and it has been possible to obtain photographs of these spectra.

One of the most interesting facts brought out by these investigations is the close resemblance between the spectra of potassium vapor and the corresponding spectra which have been observed in the case of sodium.

During the early part of the experiments the vapor was investigated in glass bulbs of from 5 to 10 centimeters diameter. A very small piece of metal was rolled up and introduced into the bulb, which was then exhausted to a vacuum of about 1 millimeter, and sealed. During a preliminary study of the conditions under which the fluorescence was exhibited to the best advantage it was found that the glass bulb became blackened after being heated for a very short time. Bulbs of hard glass, blown in an oxyhydrogen flame were then tried and found fairly satisfactory.

FLUORESCENT SPECTRUM.

Method and Apparatus. — The fluorescent light of the vapor was first examined with a two-prism Steinheil spectroscope. The spectrum showed a broad bright band with apparently no structure far out in the red. In order to obtain greater dispersion the light was next examined by means of a large three-prism spectrograph. With this apparatus the spectrum showed some structure. Examined visually about fifteen bands could be distinguished. By studying the condition carefully it was finally possible to get the fluorescence bright enough to yield fairly satisfactory spectrograms on the new Wratten & Wainwright panchromatic plates with exposures of from two to three hours.

The best photograph taken with a width of slit such that the *D* lines were just resolved on the plate showed that the spectrum was fluted, the flutings, however, not being resolved in the lines. The bands were quite sharp on the sides toward the shorter wave-lengths and on the other sides terminated in wings which extended with gradually decreasing intensity up to the head of the next band.

The absorption spectrum photographed with the same apparatus was found to be the complement of the fluorescent spectrum. When the two negatives were superimposed it was seen that each dark band of the latter was represented by a light band in the former. As it was desirable to work with a much denser vapor than it was possible to obtain with the glass bulbs, the behavior of the metal when heated in a highly exhausted steel tube was studied.

A small piece of metallic potassium was placed at the center of a piece of thin steel tubing, 2 inches in diameter and 24 inches in length. The ends were closed with glass plates, cemented to the tube with sealing wax, and the whole exhausted with a Fleuss pump, through a small lateral tube, brazed into the steel wall.

Arc-light, sent in a slightly oblique direction, was brought to a focus by means of a lens directly over the metal. On heating the tube the red spot of fluorescent light was observed through the opposite end.

The fluorescence was much more intense than had ever been observed with the vapor in the glass bulb, being of about the intensity and color of a Bunsen flame heavily charged with pure lithium chloride.

The arrangement of the apparatus during the subsequent experiments on the fluorescence was exactly similar to that employed in the work on sodium vapor. The apparatus consisted of a tube of thin steel 3'' in diameter and 30'' in length containing a steel retort, made by fitting two circular disks of steel to a short piece of tubing, slightly smaller than the long tube. The ends of the retort were provided with small oval apertures. The metal was cut up into strips and introduced into the retort, which was pushed to the center of the tube and the plate glass ends cemented on. The tube was then exhausted to a pressure of 1 mm. and heated at its center with a Bunsen flame. The illuminating beam of arc-light was brought to a focus just inside of one of the apertures of the retort. By sending the exciting light in an oblique direction through one end, the fluorescence could be observed through the same end against a dark background. With the metal in the retort, which prevented its rapid distillation to the colder parts of the tube, it was possible to make exposures of practically any length. The ends

of the tube were kept cool by jackets of absorbent cotton, which dipped into pails of water.

By employing higher dispersion an attempt was made to break up the bands which had been photographed with the three-prism spectrograph. The prisms were removed from that apparatus and a plane grating substituted. It was found that this new apparatus gave a first order spectrum about five times as long as the spectrum given by the prisms. The lenses used were of 36-inch focal length. The adjustment was so made that the center of the spectrum fell at the axis of collimation and very good definition was obtained throughout.

With this arrangement of things several very good photographs of the spectrum were obtained. The time of exposure varied from two to three hours. It was possible to measure on the dividing engine the wave-lengths of about fifty lines by comparing them with standard lines in the iron spectrum. They extend from wave-length 6346 to 6767. It was found that the centers of these bands could be determined to within half an Ångstrom unit. In the region of shorter wave-lengths the bands are all of about the same intensity, and are nearly equally spaced along the spectrum. Between 6415 and 6670 there are eight very strong lines which are about equally distant. They are represented in the magnetic rotation spectrum and are due to the strongest lines in the absorption spectrum. This series will be discussed further under the magnetic rotation spectrum. As we go out into the region of longer wave-lengths the spectrum consists of groups of lines of nearly the same intensity, the lines between the groups becoming fainter and fainter. The lines of this spectrum coincide line by line with the principal lines in the absorption spectrum, although as will be seen, there are a great many more absorption lines. The wave-lengths of the fluorescence lines measured are given below.

We have seen that, considered roughly, the fluorescent spectrum covers the region of absorption. An attempt was made to study the relation between the wave-length of the absorbed and emitted light by means of a Fuess monochromatic illuminator. This apparatus enables one to isolate a region of any width from a continuous spectrum, and to focus this light on the vapor.

Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ
6346.1	6461.0	6560.0	6657.0
6354.8	6664.4	6568.4	6663.5 strong
6364.8	6474.7	6576.0	6670.1 "
6374.4	6483.6	6584.2 very strong	6677.2 "
6383.9	6490.8	6590.4	6678.0
6393.7	6495.1	6593.0	6682.4
6400.7	6499.6	6596.5	6709.0 strong
6407.3	6508.0	6605.9	6715.8 "
6415.9 strong	6514.8	6615.2	6722.0 "
6423.7	6521.5	6624.3 strong	6748.2 "
6430.6	6527.9	6630.9 "	6761.9 "
6437.7	6537.1	6636.4	6667.6 "
6443.8 strong	6544.4 very strong	6641.6	
6453.9	6552.6	6648.9	

The method was to find by changing the wave-length of the exciting light the region of absorption which gave the maximum intensity of fluorescence, and by narrowing the slit of the illuminator as far as was consistent with the observation of the fluorescence, to isolate if possible an approximately monochromatic source of excitation. The wave-length of the exciting light was increased by turning the graduated screw which rotated the prism of the instrument, and it was found that there was a wide region which would excite the fluorescence. The spectrum examined with the Steinheil spectroscope was, however, so feeble as to be hardly observable and little was derived from this method of study.

The zinc arc was then tried as a monochromatic source. The light from the arc formed in air between a carbon electrode and a small crucible into which pieces of zinc were fed, was brought to a focus just within the aperture of the retort containing the metal. This arc gave a very intense and strongly concentrated source of light, from which the single line 6363 was utilized. It was found that a strong fluorescence was excited by this line. Examined visually with a grating spectroscope a series of lines apparently equally spaced along the spectrum was observed, analogous to the series excited in sodium vapor by the blue cadmium line 4800.

The great difficulty of working with the arc in air is that the position of the crater changes constantly, making it almost impossible

to keep the spot of fluorescent light on the slit of the spectrograph for any length of time. The spectrum of the fluorescent light brought out by exciting with the zinc arc has not yet been photographed.

ABSORPTION SPECTRUM.

The photographs of the absorption spectrum taken with the vapor in the bulb never showed very strong absorption for the reason that it was impossible to get the vapor sufficiently dense. With the steel tube it was possible to work with a very dense vapor, and with the greater dispersion given by the grating spectrograph, excellent photographs have been taken of the absorption spectrum.

A lump of potassium was placed at the center of the tube, the ends were cemented on and the tube exhausted as in the previous experiments. The tube was supported in a horizontal position in front of the slit of the spectrograph, and light from the arc sent through the tube was brought to a focus on the slit. By regulating the flow of gas to the burner, placed below and at the center of the tube, it was possible to observe the spectrum for any degree of density of the vapor. Photographs were taken at different densities. The heads of the bands appear first, and as the density increases the fine lines of which they are formed develop in succession. With a sufficiently dense vapor the spectrum consists of a very large number of fine black lines. The wave-lengths of the strong bands and principal lines of the absorption spectrum are given below.

Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ	Wave-Lengths. λ
6295.2	6399.7	6549	6675.1
6298.5	6412.5 strong	6559	6677.7
6306.8 strong	6420.3 "	6565.6	6709
6321.7	6433.8	6583.9 very strong	6714.5 strong
6324.6 strong	6443.3 very strong	6594.2	6721.4
6334.3 "	6466.8 " "	6605.0	6754.4
6343.3 "	6488.9 strong	6611.3	6759.9
6354.0 "	6505.3 "	6622.7 strong	6765.8
6362.9 very strong	6512.8 "	6629.4	6804.9
6370.1	6520.3 "	6641.2	6811.4
6382.9 very strong	6534.6	6662.7 strong	6849.9
6391.3	6544.3 very strong	6668.5 "	6855.5

MAGNETIC ROTATION SPECTRUM.

Method and Apparatus.—The magnetic rotation properties of potassium vapor were first investigated in the following way: A glass bulb which had been filled, exhausted and sealed off was suspended between the conical pole pieces of a large electromagnet. Light from an arc lamp rendered parallel by a lens was passed in succession through a nicol prism, the hollow cores of the magnet with the bulb containing the metal, and a second nicol, after which it was brought to a focus by a second lens on the slit of the grating spectroscope. The nicols were set for complete extinction of the light so that the field was dark. The bulb was heated by a Bunsen flame until the metal was vaporized, and the magnet excited. On looking into the spectrograph a faint yellow light was observed in the vicinity of the D lines due to rotation by traces of sodium vapor. No rotation lines in the red were observed. On repeating the experiment, however, with the vapor in a steel tube, a bright line rotation spectrum was discovered.

A piece of steel tubing of such diameter as to slip through the hollow cores of the magnet from which the conical pole pieces had been removed was charged with potassium and exhausted. Parallel light was sent through the tube, nicols, etc., as described above, and focused on the slit. With the current off the height of a flame placed beneath the center of the tube was regulated so that the absorption lines were brought out strong and black. The nicol was then set for complete extinction. On exciting the magnet there appeared in addition to the bright rotation lines D_1 and D_2 a number of bright lines in the red. It was found that the rotation spectrum was very sensitive to changes in the density of the vapor. The least variation in the height of the flame would destroy the spectrum. Electrical heating of a porcelain tube containing the metal was tried, but it was found that the density could be kept more constant by working with a steel tube and heating with a flame.

Several photographs of the rotation spectrum were taken. About twenty-five lines could be measured on the best plate. One was taken with the absorption spectrum on the same plate and shows the eight strong lines which were mentioned in connection with the fluorescent spectrum. The plate shows that they coincide with the

strong heads of the absorption bands. Six of these strong lines could easily be picked out as a series of lines, very nearly equidistant along the spectrum. Their wave-lengths are :

λ		λ Differences.
6383.02		
6412.71		29.69
6443.4		30.69
6474.21		30.81
6505.06	60.54	30.85
6565.6	$\frac{2}{2}$	30.27

There are three strong lines which do not fall in this series :

6512.67	6543.88	6583.32
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The other lines are all of about the same intensity. Their intensities do not depend upon the intensities of the corresponding absorption lines, a fact which was found to hold in the magnetic rotation spectrum of sodium vapor. Some of the strongest lines in this region show no rotation. The wave-lengths of the lines that could be measured are as follows :

λ	λ
6298.63	6443.4 strong
6306.86	6474.21 "
6313.29	6489.69
6325	6505.06 strong
6329.23	6512.67 "
6342.81	6543.88 "
6351	6556.5
6354.77	6565.61 strong
6383.02 strong	6583.32 "
6391.13	6601.7
6412.71 strong	6614.6
6420.43	6622.35

The results obtained up to the present time can only be considered as preliminary in their nature. The vapor of potassium resembles that of sodium in its optical properties, but its study is attended by far greater difficulties. The banded absorption spectrum which gives rise to the fluorescence is located with respect to the first doublet of the principal series 7699 and 7665 in very much the same way as the sodium absorption spectrum is located with respect to the *D* lines. The marked resemblance in the

appearance of the spectra has been mentioned. Further work will doubtless show us ways of overcoming some of the difficulties, although it is very doubtful if we can ever handle the vapor with the same facility as is possible in the case of sodium, for there are very few sources of monochromatic red light available.

Careful study of the magnetic rotation spectrum will probably be more profitable, especially an investigation with the Fresnel double quartz wedges, which enable us to determine the direction of the rotation at each absorption band.

BIOGRAPHICAL NOTE.

Taylor Scott Carter was born near Marshall, Virginia, on the 8th of July, 1881. He received his early education under a private tutor at his home, and in the fall of 1896 he entered Bethel Military Academy near Warrenton, Va., where he remained one year, and then matriculated at the Virginia Military Institute, from which institution he was graduated in June, 1901, with the degree of Bachelor of Science. The next year he was instructor in Physics and Mathematics at the New Mexico Military Institute, Roswell, N. M. In the fall of 1902 he was appointed Assistant Professor of Mathematics and Mechanical Drawing at the Virginia Military Institute. He entered the graduate department of Physics at the Johns Hopkins University in the fall of 1904, taking Physical Chemistry and Mathematics as first and second subordinates respectively. During his course at the University he pursued his studies in Physics under Professors Ames, Wood and Bliss ; in Applied Electricity under Dr. Whitehead ; in Physical Chemistry under Professor Jones ; and in Mathematics under Dr. Cohen. He held a Hopkins Scholarship from Virginia during his three years residence at the University.

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED

WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS

ERNEST MERRITT, AND FREDERICK BEDELL

Two volumes of THE PHYSICAL REVIEW are published annually, these volumes beginning in July and January, respectively, and containing six numbers each. The price of subscription is two dollars and fifty cents a volume (five dollars a year), or fifty cents a single number, seventy-five cents double number. Subscriptions should be sent to the publishers, THE MACMILLAN COMPANY, 41 *North Queen Street, Lancaster, Pa.*, or 66 *Fifth Avenue, New York*; Messrs. MACMILLAN & CO., LTD., *London*; or to Messrs. MAYER AND MUELLER, *Berlin*.

THE PHYSICAL REVIEW beginning with Vol. XVI. (January-June, 1903) is conducted with the co-operation of the AMERICAN PHYSICAL SOCIETY. The separate publication of the BULLETIN of the Society has been discontinued and its Proceedings are hereafter to be published regularly in the REVIEW.

Previous to Volume V. (July-December, 1897) THE PHYSICAL REVIEW was published in annual volumes, each containing six bi-monthly numbers, beginning with the July-August number, 1893. These may be obtained from the publishers at the former subscription price, three dollars per volume.

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Entered at the post-office, at Lancaster, Pa., as second-class mail matter.

